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Kinetics and Mechanisms of the Oxidation of Ni(II) and Cu(II) Macrocycles by Aquasilver(II) in Acidic Perchlorate Media

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Abstract

The oxidation of Ni^{II}cyclam, Cu^{II}cyclam (cyclam = [18]aneN$_4$) and Cu^{II}CT (CT = Me$_6$[14]-4,11-dieneN$_4$) by aquasilver(II) has been investigated kinetically in perchlorate media in the range [$HClO_4$] = 1–4 mol dm^{-3}. The reaction stoichiometry indicates 1 mol of oxidant reacting with 1 mol of M(II). Stopped-flow studies indicate a single reaction pathway involving $M^{II}L + Ag^{2+}$ with $k = 2.3 \times 10^5$, 3.5×10^5 and 1.5×10^4 dm^3 mol^{-1} s^{-1} for Ni^{II}cyclam, Cu^{II}cyclam and Cu^{II}CT respectively, at 10 °C. While Ni^{III}cyclam is stable enough to allow UV–Vis characterization, Cu^{III}cyclam and Cu^{III}CT decay by a first-order process with rate constants of 1.5 and 0.053 s^{-1} respectively. Reliable kinetic results could not be obtained for the oxidation of Ni^{II}CT by silver(II), but the oxidation product does, like Ni^{III}cyclam, have a significant lifetime.

Introduction

Tetraazamacrocyclic complexes containing trivalent nickel [1] and copper [2] have been prepared by electrochemical, chemical, pulse radiolytic and photochemical means. In aqueous solution in the absence of stabilizing axial ligands, tetradentate complexes show a large spread of redox potential and kinetic stability depending on the particular systems involved. In order to characterize such properties, we have begun a kinetic study of the oxidation of nickel(II) and copper(II) macrocyclic tetraaza complexes by a strong oxidizing agent, namely the aquasilver(II) ion, and of the decomposition of the intermediate $M^{III}L$ species. This type of chemical route enables the production of complexes which may not be amenable to electrochemical study because of interference of the water wave.

We report here on the reactions between aquasilver(II) and the copper(II) and nickel(II) complexes of [14]aneN$_4$ (cyclam) and Me$_6$[14]-4,11-dieneN$_4$ (CT). Under the acid conditions required for the stabilization of Ag^{2+}, the oxidized nickel complexes are metastable. The analogous Cu(III) species have recently been stabilized [3] in 10 mol dm^{-3} acid but decompose rapidly even when [H^+] = 4 mol dm^{-3}. This difference seems to be because the copper(III) complexes undergo intramolecular electron transfer with resulting ligand fragmentation and release of free Cu(II) [4].

The square-planar environment imposed by the macrocyclic ligands and the low-spin configurations suggest an outer-sphere redox mechanism. This has been confirmed for example by McAuley in the reaction of Co(III) with Ni^{II}cyclam [5]. Square-planar copper(III) complexes should be completely noncoordinating at axial sites. Margerum has found, however, that a large number of reactions involving both the $Cu^{III,II}$ and $Ni^{III,II}$ couples react by an inner sphere mechanism [6–8].

Experimental

Materials

Silver(I) perchlorate solutions were obtained by dissolving Ag_2O in a known excess of $HClO_4$. Ag(II) was generated by anodic oxidation in 1–4 mol dm^{-3} $HClO_4$ in the presence of 0.1 mol dm^{-3} Ag^+ (to prevent disproportionation) [9]. Its redox potential in 1.0 mol dm^{-3} $HClO_4$ is 2.0 V [9].

Metal–macrocycle complexes were prepared by reaction of the ligand with a 1–2% excess of Ni(II) or Cu(II) perchlorate. Neutral stock solutions were diluted and acidified just before use.

Procedure

Kinetic experiments were performed on a Durrum stopped-flow apparatus (model D-110) interfaced to an Apple II microcomputer. Reactions were monitored at a variety of wavelengths as an increase in absorbance due to oxidation of the macrocyclic

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complex. Spectra were recorded on a Varian Cary 219 spectrophotometer.

Most kinetic experiments were performed at 10 °C in order to allow a full variation of reductant concentration while keeping the faster reactions within the time scale of the stopped-flow apparatus. For reactions where the decomposition of the oxidized macrocycle was on a similar time scale to the initial redox reaction, the rate constant for the first step was evaluated for the initial part of the curve (1.5 half-lives) with adjustment of the limiting absorbance where appropriate. Otherwise, all reactions obeyed fist-order kinetics for at least three half-lives.

Results and Discussion

For all four reactions, oxidation of the divalent metal complex by silver(II) resulted in a substantial increase in spectral intensities in the visible and ultraviolet. Thus, we were able to maintain low Ag(II), high excesses of reducing agent, and still keep all reaction rates within the range of the stopped-flow apparatus. Long-lived metastable complexes with spectra matching those reported for Ni^{III}cyclam and Ni^{III}CT were observed for the nickel(II) oxidations [4, 10]. The spectrum of $nickel^{III}$cyclam is reproduced in Fig. 1. Since accurate spectral measurements were possible for these systems, a redox stoichiometry could be determined. In both cases $\Delta[Ag(II)]/\Delta[Ni(III)]$ was equal to unity within a few percent.

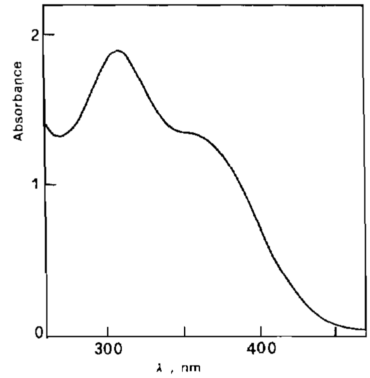

Fig. 1. UV–Vis spectrum of a solution produced by reaction of excess Ni^{II}cyclam with 1.8×10^{-4} mol dm^{-3} silver(II) [$HClO_4$] = 1.0 mol dm^{-3}; ionic strength = 4.0 mol dm^{-3}.

For both the copper systems, a steady increase in absorptivity was observed in the stopped-flow apparatus as the wavelength decreased from 450 to 350 nm. This corresponds nicely to the transient observed in the oxidation of Cu^{II}CT by OH· and Cl_2^- radicals (maximum at 315 nm) [11] but differs from the transient Cu^{III}cyclam spectrum measured by Zeigerson *et al.* at pH 3.2 (maximum at 400 nm) [4]. We note that the stable Cu^{III}CT species formed in 10 mol dm^{-3} acid [3] and in CH_3CN [2] has absorption maxima near 330 and 400 nm. The sensitivity of the spectra of copper(III) complexes to the environment (including medium, ligand configuration and electronic distribution) has been discussed elsewhere [4, 12], and we must conclude that, in particular, the product of the Ag(II)–Cu^{II}CT reaction differs from Cu^{III}CT produced electrochemically.

Kinetics of the redox reaction were uniformly pseudo-first-order in M(III) formation and, hence, Ag(II) disappearance. The M(II) dependence was found to be first-order for Cu^{II}cyclam, Cu^{II}CT and Ni^{II}cyclam. These reactions were also [H^+] independent. The experiments with Ni^{II}CT suffered from a lack of reproducibility, perhaps because of a high sensitivity to impurities, light, or free metal ions. The decomposition rates for the unstable Cu(III) intermediates were first-order in [Cu^{III}L] and independent of [Cu^{II}L] and [H^+]. Rate data for the Cu–cyclam and Cu–CT systems are listed in Table I. A summary of kinetic results for all systems is given in Table II.

TABLE I. Pseudo-first-order Rate Constants for the Oxidation of Cu^{II}cyclam and Cu^{II}CT by Ag(II). [Ag(I)] = 0.10 mol dm^{-3}; [Ag(II)] < 1×10^{-5} mol dm^{-3} (reaction progress monitored at 400 nm)

[$HClO_4$] (mol dm^{-3})	10^4 [Cu^{II}L] (mol dm^{-3})	k_{obs} (s^{-1})		T (°C)
		oxidation	decomposition	
Cyclam				
1.0	10.0		1.38	10
1.0	5.0	122	1.46	10
1.0	3.0	76.5		10
1.0	2.0	41.1	1.65	10
1.5	2.0	46.0	1.44	10
2.0	2.0	38.5	1.32	10
4.0	2.0	44.5	1.52	10
1.0	1.0	23.9	1.41	10
1.0	0.8	21.7	1.55	10
1.0	0.6	17.6	1.47	10
1.0	0.4	8.0	1.51	10
1.0	2.0		2.50	20
1.0	1.0		2.78	20
CT				
1.0	2.0	2.93	0.059	10
1.0	1.0	1.39	0.047	10
4.0	1.0	1.46	0.053	10
1.0	0.8	1.20	0.047	10
1.0	0.6	0.96	0.058	10
1.0	0.4	0.78	0.051	10
1.0	2.0	4.80	0.11	20
1.0	1.0	2.3	0.10	20

TABLE II. Summary of the Derived Rate Constants

Reductant	T (°C)	k_{ox} ($dm^3\ mol^{-1}\ s^{-1}$)	k_{decomp} (s^{-1})
Cu^{II}cyclam	10	3.5×10^5	1.5
	20		2.6
Cu^{II}CT	10	1.5×10^4	0.053
	20	2.4×10^4	0.10
Ni^{II}cyclam	10	2.0×10^5	$t(1/2) > 100$ min
Ni^{II}CT	10		$t(1/2) > 50$ min

As can be seen from Table II, the intermediate trivalent species is sufficiently long-lived on the time scale of the stopped-flow experiment to enable the detection of both formation and decomposition. Specific rate constants for copper point out that the rates of both copper^{II}–cyclam oxidation and of the subsequent decomposition are more than one order of magnitude higher than for the corresponding Cu–CT complex. This oxidation rate follows the same trend as the half-wave potential values (1.05 V for $Cu^{III/II}$cyclam and 1.19 V for $Cu^{III/II}$CT).*

In the case of the decomposition reaction, thermodynamic data would suggest a higher kinetic stability for Cu^{III}cyclam, but this is contrary to observation. Such an inverted decomposition rate has been observed with other metal macrocycles [11, 4]. In the case of nickel, the oxidation step for the nickel–cyclam complex could be measured on the stopped-flow apparatus, while the reaction of nickel–CT could not be reliably determined even though the redox potentials (0.84 V for cyclam and 1.16 V for CT) [13] suggest a slower rate.

An inverse hydrogen ion dependence in the reaction between Ni^{II}Cyclam and Co(III), indicates that the $CoOH^{2+}$ ion is the principal oxidant and suggests the possibility that initial redox might involve a hydrogen atom extraction [5]. In the present systems, the absence of a kinetic dependence on $[H^+]$ (Table I) is an indication that $AgOH^+$ is not the predominant reactant. Noting that at 10 °C, where $K_h = 0.15$ mol dm^{-3} [9], Ag^{2+} comprises over 85% of the total silver, we may conclude that the reactivity of $AgOH^+$ is similar to, or perhaps somewhat less than that of Ag^{2+}_{aq}.

As a test of the possible outer-sphere nature of the three reactions for which oxidation rates were determined, we have applied the Marcus cross relationship [14]:

$$k_{12} = (k_{11} k_{22} K f)^{0.5} \qquad (1)$$

$$\log f = (\log K)^2 / 4 \log(k_{11} k_{22} / Z^2) \qquad (2)$$

where K is the equilibrium quotient of the redox cross reaction, Z is the collision frequency in solution 10^{11} s^{-1}, and k_{11} and k_{22} are the self-exchange rate constants for the redox couples of each reagent, to see if consistencies between the kinetic data for the oxidation of Ni(II) and Cu(II) macrocyclic complexes could be checked.

Using the value 2×10^3 $dm^3\ mol^{-1}\ s^{-1}$ for the self-exchange rate of the $Ni^{III/II}$ cyclam couple [15] and the above assuemed redox potentials in order to compute the corresponding K value, we calculate from eqn. (1) (after successive iterations in order to account for the f factor) a value of the self-exchange rate of $k_{22} = 2 \times 10^{-9}$ $dm^3\ mol^{-1}\ s^{-1}$ for the $Ag^{2+/+}$ couple. This value seems abnormally low and may reflect the inner-sphere tendency for redox reactions of $Ni^{III/II}$ macrocyclic ligand complexes [6–8]. We must point out, however, that this value is very close to the one derived from the cross reaction rate between Ag(II) and Fe(II) [16]; in addition an inner-sphere mechanism for Ni(III) macrocyclic complexes seems reasonable for reactions with cyano complexes or other anionic reactants, while it seems less likely for the reaction with aquasilver(II).

The use of the derived self-exchange rate constant for $Ag^{II/I}$ enables the evaluation of k_{11} for $Cu^{III/II}$ cyclam, using the rate for the cross reaction Cu(II)-cyclam + Ag(II) obtained here and the redox potentials reported above. The derived value is 8×10^7 $dm^3\ mol^{-1}\ s^{-1}$. This value seems to be abnormally high when compared with the behaviour found for other $Cu^{III/II}$ peptide complex couples [8].

The results obtained from such computations appear to point out a failure of the Marcus cross relationship for the present reactions for which an inner-sphere contribution is likely to be operative.

Another inconsistency comes out by computing the rate constant for the reaction Ag(II) + Cu(II)CT, assuming for the $Cu^{III/II}$CT couple the same self-exchange rate as for the cyclam complexes, and using the self-exchange rate for $Ag^{II/I}$ and the redox potentials reported above; the computed rate constant for the reaction Ag(II) + Cu(II)CT is 2.7×10^5 dm^3 $mol^{-1}\ s^{-1}$ which is not in agreement with the experimental value reported in Table II.

The results of these comparisons indeed suggest that these are not simple outer-sphere reactions. Similar conclusions have been drawn for the reaction of Ag^{2+} with uncomplexed metal ions [16]. Possible inner-sphere contributions to the investigated redox reactions and other effects such as non adiabaticity of the electron transfer could be responsible for such behaviour [16].

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*These values have been assumed considering those determined by Fabbrizzi *et al.* [3] at $[HClO_4] = 10$ mol dm^{-3}, and taking into account the effect of ionic strength (predominant with respect to acidity) on $Cu^{III/II}$ and $Ni^{III/II}$ macrocyclic couples of similar structure (see ref. 13).

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